Identifying evidence for past mining and metallurgy from a record of metal contamination preserved in an ombrotrophic mire near Leadhills, SW Scotland, UK.

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Keywords: peat; lead, stable isotope analysis, Leadhills, Wanlockhead, mining

Abstract

This study presents a new 3600-year record of past metal contamination from a bog located close to the Leadhills and Wanlockhead orefield of south west Scotland. A peat core, collected from Toddle Moss, was radiocarbon (^{14}C) dated and analysed for

trace metal concentrations (by EMMA) and lead isotopes (by ICP-MS) to reconstruct the atmospheric deposition history of trace metal contamination, in particular lead. The results show good agreement with documented historical and archaeological records of mining and metallurgy in the region: the peak in metal mining during the eighteenth century, the decline of lead mining during the Anglo-Scottish war and lead smelting during the early medieval period. There may also have been earlier workings during the late Bronze and Iron Ages indicated by slight increases in lead concentrations, the Pb/Ti ratio and a shift in $^{206/207}$Pb ratios, which compare favourably to the signatures of a galena ore from Leadhills and Wanlockhead. In contrast to other records across Europe, no sizeable lead enrichment was recorded during the Roman Iron Age, suggesting that the orefield was not a significant part of the Roman lead extraction industry in Britain. These findings add to the various strands of archaeological evidence that hint at an early lead extraction and metallurgical industry based in southern Scotland. The results also provide further evidence for specific regional variations in the evolution of mining and metallurgy and an associated contamination signal during prehistoric and Roman times across Europe.

Introduction

Since its first use approximately seven millennia ago, lead has played an important role in human history, including aspects of art, medicine and technology (Hong *et al*., 1994; Nriagu, 1998). Lead became particularly important in the fifth millennium BC with the discovery of new smelting and cupellation techniques for lead-silver alloys and by Roman times the use of lead was widespread (Ngriau, 1983; 1996). At

present there is a paucity of archaeological evidence for lead mining in prehistoric Britain. It has been proposed that lead deposits in Wales, and by inference elsewhere in Britain, were exploited for lead and silver, since the location of most of the prehistoric mines (where copper was the main target) mostly occur in places with a long tradition of lead and zinc mining (Bick, 1999). Evidence of limited working of the lead veins and crushing of ores at the Bronze Age mine of Copa Hill in central Wales (Timberlake, 2003) provides some tentative evidence for the extraction of lead ore approximately 300-500 years before its use in metalwork, a phenomenon that might represent a period of metallurgical experimentation rather than actual production (Timberlake, 2003).

Lead in Bronze Age artefacts confirms that it was being used in Britain prior to 1500BC and hints at the probable early exploitation of insular sources and trade in metal ore (Rohl and Needham, 1998). A smelted lead bead necklace in an early Bronze Age grave was found in southeast Scotland (Hunter and Davis 1994), and other early lead finds have been reported from Cornwall (Shell, 1979) and Co. Tipperary (Rafferty, 1961). Lead was also intentionally being alloyed with copper and tin to produce bronze by the Middle-Late Bronze Age (Tylecote, 1986; Rohl and Needham, 1998). Small pieces of lead have also been found in late Bronze Age occupation sites (e.g. Needham and Hook, 1988). The precise sources of this lead remain a matter for speculation (Barber, 2003).

Archaeological evidence for lead extraction, objects and its wider use in later prehistory is also scant. Lead was a rare addition to northern British alloys during the

Iron Age (Dungworth, 1996) and only a few examples of lead use in ornaments, or as solder to secure iron objects, exist in Scotland (Toolis, 2007). Roman lead extraction and smelting is more abundant, with known mines and/or smelting sites occurring at Charterhouse in the Mendips, SW Britain, Alderley Edge in Cheshire and sites in Wales (Timberlake et al., in press), but so far there are no known sites in Scotland. One region that has been not fully investigated is the Leadhills and Wanlockhead orefield in SW Scotland. A study is therefore warranted, especially given the recent discovery of a stone hammer in Wanlockhead, which is indicative of early mining (Pickin, 2008).

The aim of this study was to reconstruct the history of exploitation of insular ore sources in the Leadhills/Wanlockhead Orefield from prehistory to the present. To do so, we present an atmospheric metal contamination history from an ombrotrophic mire, Toddle Moss, for the last 3200 years using total concentrations, Pb/Ti ratios and lead isotope ratios ($^{206}Pb/^{207}Pb$) contained in the peat.

Materials and methods

Location, sampling and sub-sampling strategy

The orefield of Leadhills and Wanlockhead, on the border of Dumfriesshire and Lanarkshire, southwest Scotland (Figure 1), is rich in metalliferous deposits as a result of two phases of mineralization in Ordovician sediments: a quartz vein mineral phase of Carboniferous age and possibly a metallic one of lead and zinc during the

Carboniferous era. This was followed by a later phase of secondary enrichment (Pattrick and Polkya, 1993*)*.

Toddle Moss is located approximately 4 km northwest of the village of Leadhills and 0.5 km east of Elvanfoot in the Elvan Water river valley (Figure 1). This area has a rich history of mining. Alluvial sediments have been worked in this valley for gold and lodes rich in lead and copper have also been exploited, particularly in the AD 1700s (Rowan et al., 1995; Chapman and Leake, 2005). Toddle Moss is an ideal site for studying past records of metal pollution because the bog is ombrotrophic ('rain fed' only) and receives inputs, including pollutants, solely from the atmosphere via precipitation and dry fallout.

A 7.5 m-deep *Sphagnum*-*Eriophorum*-rich peat core was taken from Toddle Moss using a Russian corer with 30 x 10 cm chamber in 2004. The samples were placed in plastic guttering, wrapped in polythene and placed in cold storage. The top 3.5 m was analysed in this study.

Chronology

Radiocarbon dates were determined at Beta Analytic Ltd (Miami) and the Poznań Radiocarbon Laboratory using conventional and Accelerator Mass Spectrometry (AMS) methods respectively. The total carbon of one sample of fresh peat (Beta-15142) was dated using conventional radiometric dating. For AMS, a 1 cm-thick slice

of peat (Poz-19215) and *Sphagnum* macrofossils (Poz-56748) were selected for dating (cf. Nilsson et al., 2001; Piotrowska et al., 2011).

To provide a highly-resolved chronology for the last 100 to 150 years, the unsupported $^{210}Pb_{un}$ activity within samples towards the peat surface was ascertained by subtraction of the supported component (measured as ^{214}Pb at 295.22 and 351.93 keV) from the total ^{210}Pb activity measured at 46.54 keV (Wallbrink et al., 2002). ^{210}Pb and ^{214}Pb activities were measured using EG&G ORTEC hyper-pure Germanium detectors in a well configuration (11 mm diameter, 40 mm depth) housed at Coventry University. The method for calculating the depth age relationship follows procedures described by Appleby & Oldfield (1978), Appleby (2001) and Walling et al. (2002). The CRS dating model was used to calculate ages as accumulation rates varied down core (Appleby et al., 1988; Appleby 2001). The CLAM software package (Blaauw, 2010) was used to create an age-depth model, combining the ^{14}C and ^{210}Pb ages, to infer approximate ages for all levels.

Geochemical analyses

The core was cut into contiguous 1 cm-thick slices, oven dried at 40^0C and homogenised to improve the efficiency of the chemical digest and to provide better representation of the total metal concentration within the samples. Calcium and magnesium were determined by ICP-OES. An estimation of the efficiency of the digestion method and of the accuracy of the analytical measurements was obtained through the use of replicate sub-samples, spiked blanks and certified reference materials (Ebdon *et al.*, 1998; Fifield and Kealey, 1998). Spiked samples of known

concentration (10 mg l^{-1}) were used to test the efficiency of the acid microwave digestion. Two certified reference materials were also used: *Sphagnum* energy peat (NJV 94-2) and *Carex* energy peat (NJV 94-1). The reference materials were imported from the Swedish University of Agricultural Sciences, Department of Agricultural Research for Northern Sweden, Laboratory for Chemistry and Biomass. Standards of known metal concentrations were used to calibrate the instrument and to ensure it was performing at its optimum efficiency (Holler *et al*. 1996). Total metal concentrations in each sample are expressed in units of μg g^{-1}.

Recovery of calcium and magnesium from the CRMs for *Sphagnum* and for *Carex* was between 101 and 130%. Three spiked samples yielded recovery of between 101 and 114%. These results suggest that metal recovery using the microwave digestion was very efficient and that the ICP-OES were providing reliable data.

The elemental composition of 89 dried, milled and homogenized samples between 0 and 300 cm depth were obtained by X-ray fluorescence dispersive EMMA-XRF analyses (Cheburkin & Shotyk, 1996; Weiss and Shotyk, 1998) including concentrations of major and trace lithogenic elements (silicon, aluminum, titanium, gallium, yttrium and zirconium), and trace metals and metalloids (lead, chromium and arsenic). The instruments are hosted at the RIAIDT (Infrastructure Network for the Support of Research and Technological Development) facility of the University of Santiago de Compostela, Spain. Standard reference materials were used for the calibration of the instruments. Quantification limits were: 0.001% for Ti; 0.01% for Al; 0.05% for Si; 0.5 μg g^{1} for Pb and 1 μg g^{-1} for the other trace elements. Replicate

measurements were taken for one every five samples in order to account for reproducibility; all replicates were within 5% agreement.

Twenty eight sub-samples of peat from the same core were selected for lead isotope analysis at the School of Geosciences, University of Edinburgh. Sub-samples (~0.25 g) were air-dried then ashed at 450°C for 4 hours, and finally digested using a modified US EPA Method 3052 Protocol microwave-assisted HF-HNO_3 digestion method (Yafa et al., 2004; Yafa and Farmer, 2006). Digests were evaporated to 1 ml on a hotplate and then made up to 25 ml with 2% (v/v) HNO_3. All reagents used in sample preparation were of the highest analytical quality available, i.e. Aristar nitric acid (69 %) and hydrofluoric acid (48 %) and high purity water (18.2 MΩ cm) from a Milli-Q water system (Millipore, Watford, UK). Lead isotopic ratios were determined in the prepared 2% v/v HNO_3 solutions using a PlasmaQuad (PQ) 3 ICP-MS instrument (Thermo Electron, Winsford, UK), equipped with a Meinhard nebulizer, nickel sampler and skimmer cones, Gilson autosampler and a Gilson Minipuls 3 peristaltic pump (Anachem, Luton, UK). A solution of the National Institute of Standards and Technology (NIST) common lead isotopic reference standard SRM 981 ($^{206}Pb/^{207}Pb$ = 1.093, $^{208}Pb/^{206}Pb$ = 2.168, $^{208}Pb/^{207}Pb$ = 2.370) was used for calibration and mass bias correction (Farmer et al., 2000). Analytical precision on these ratios was typically < ±0.2%.

To ensure the quality of analytical procedures and data, an ombrotrophic peat reference material (NIMT/UOE/FM001) [Yafa et al., 2004] was analysed along with the samples. The mean values (n=5) of 1.177±0.001, 2.093±0.002 and 2.463±0.004

determined for the isotope ratios $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$ and $^{208}Pb/^{207}Pb$, respectively, in the reference material were in good agreement with corresponding "information only" values of 1.176 ± 0.001, 2.092 ± 0.002 and 2.461 ± 0.003 reported in Yafa *et al*. (2004).

Statistics

Following the procedure described by Martínez-Cortizas et al. (2013) and Hermanns & Biester (2013), we used factor analysis by Principal Components (PCA) to identify sources and processes related to the distribution of the measured elements using the SPSS 20 software package. PCA of compositional data is usually undertaken on transformed variables (Baxter, 1995), particularly when the values cover several orders of magnitude and there are outliers (Baxter, 1999). Transformation also avoids any scaling effects (Eriksson et al., 1999). Thus, the PCA was done on log-transformed and standardized (z-scores) data, using varimax rotation to maximize the variance of the elements in the Principal Components (Eriksson et al., 1999). Similarly distributed elements will load on to the same Principal Component and are most likely to be controlled by the same environmental factor(s). Hence, interpretation of the signals with regard to the underlying cause or causes of variation of a group of elements should be more evident.

Results

Age-depth modelling

The results are shown in Table 1 with 2 σ calibrated age ranges (in calibrated years BC/AD). A polynomial regression age-depth model is shown in Figure 2. All dates

appearing in the following text are cited in calendar years BC/AD, unless otherwise stated, and are given within the 95% confidence intervals derived from the Calib 7.0 model, with end-points rounded to the nearest decade.

Geochemistry

The calcium-magnesium ratio (Figure 3) is consistently below 1 and much lower than the measured value for rainwater (approximately 1.9) at Raeburn Flow, which is located approximately 74 kilometres to the south east of Toddle Moss (Küttner et al., 2014). These low values are sufficient to infer ombrotrophic conditions for the bog (cf. Shotyk, 1996). Notwithstanding a series of short-lived peaks, titanium concentrations remain relatively constant from the base of the profile to 101 cm. They then rise gradually with a sustained increase from 43 cm to the surface of the bog. Lead concentrations are generally low from the base of the core to 35 cm depth: thereafter they increase dramatically to peak at 11 cm before decreasing to much lower concentrations at the bog surface. The Pb/Ti ratio follows a similar pattern. The $^{206}Pb/^{207}Pb$ profile shows more radiogenic ratios from 342 cm to 308 cm (SI Table 1). A shift to less radiogenic values occurs between 308 and 222 cm (Figure 3). Thereafter the ratios gradually rise from 222 cm to 24 cm before they become less radiogenic towards the bog surface.

Concentrations of arsenic, chromium, gallium, yttrium, zinc and zirconium, determined using EMMA, are shown in Figure 4. Arsenic, gallium and yttrium have similar trends to lead: low concentrations from the base of the core until 35 cm, a sharp rise to peak in the top 10 cm, followed by a decline to much lower

concentrations. Zinc and chromium are characterised by low but highly fluctuating concentrations from the base of the core until approximately 80 cm. They also peak in the uppermost 10 cm with the other elements. Chromium concentrations also decline close to the peat surface but zinc remains relatively high. Zirconium concentrations are more erratic with a series of peaks throughout the profile (e.g. 265, 237, 179, 135, 113, 63, 33 and 17 cm) but show a gradual increase in the upper metre of the profile.

Principal Components analysis

Two components explain 78% of the total variance (Table 2). The first component (Cp1, 44% of the total variance) is characterized by large to moderate positive loadings of metals typically associated with mining/metallurgy (namely arsenic, zinc, lead and chromium; Table 2). Gallium and yttrium , which are usually considered to be lithogenic elements, show large loadings in Cp1 (Table 2) and can thus can also be associated with atmospheric metal pollution, they probably derive from dust emissions during mining. This is also supported by the extremely high metal concentrations in the upper section of the peat, which are only comparable to those found close to pollution sources (e.g., inthe Harz mountains, Germany, where Pb concentrations, exceed 1000 µg g^{-1} during medieval times [Kempter and Frenzel, 2000] and equivalent to lead concentrations determined within several kilometres of a lead smelter [Mihaljevič et al., 2006]). Cp1 scores show a typical record of atmospheric metal pollution, with a large peak in the upper 30 cm of the core and a sharp decrease in the upper 8 cm (Figure 5). It also shows two minor increases in scores during the early medieval period: between 120 and 140 cm (5th-7th centuries

AD) and from 90 to 100 cm (9th-11th centuries AD).

The second component (Cp2, 33.7% of the total variance) is characterized by large positive loadings of the lithogenic elements (Ti, Si, Al, and Zr; Table 2). This chemical association reflects the mineral content of the peat due to deposition of dust, probably derived from soil erosion. The record of scores shows a 'see-saw' pattern, with eight peaks in dust deposition (Figure 5): at 265 cm (c. 870 cal BC), 237 cm (c. 560 cal BC), 179 cm (c. 70 cal BC), 133 cm (c. AD 570), 109 cm (c. AD 835), 85 cm (c. AD 1095), 63 cm (c. AD 1335), and 33 cm (c. AD 1660). Although most of the variation in the concentrations of the metals is related to the first component (i.e. atmospheric metal pollution), a small proportion of the changes in lead, arsenic, gallium and yttrium are also correlated to Cp2 (Table 2) and therefore they indicate a geogenic contribution.

Due to the expected large effect on the PCA of the metal concentrations of the peat sections with ages younger than AD 1600, we performed a second PCA using only the data for peat sections with pre-industrial ages (below 38 cm). In this data set the first component, Cp1-PI, is characterised by the large loadings of the lithogenic elements (silicon, titanium, aluminum, yttrium and zirconium; Table 2). Cp1-PI and Cp2 scores are highly correlated (r 0.97). Most of the yttrium variance is now in this component, suggesting that in Toddle Moss its association with the metals associated with pollution occurs only after the start of the Industrial Revolution. This is not the case for gallium, whose variance is still loaded into a metal component (Table 2).

Moreover, in the second analysis, the metal signal is divided into two components: Cp2-PI with zinc, arsenic and chromium which has a record of scores similar to that of Cp2 (r 0.68), and Cp3-PI with gallium and lead (Table 2). Thus, the metal signature of the peat for pre-industrial times seems to indicate that there were differences in the accumulation of the metals in Toddle Moss. The record of Cp2-PI scores suggests that the history of zinc, arsenic and chromium enrichment is quite similar during late prehistory and early Middle Ages. However, the elevated scores of Cp2-PI between 250 and 236 cm, corresponding to the period c. 700-550 cal BC, is not paralleled by lead.

Interpretation and Discussion

Lead is essentially immobile once it becomes incorporated into ombrotrophic peat (Mackenzie et al., 1997; Shotyk et al., 1997) and there is a plethora of studies that have demonstrated that the pattern of lead is faithfully preserved in peat bogs which can be reliably matched with other archaeological and historical documentary records (e.g. Shotyk et al., 1997; Mighall et al., 2002b). Lead concentrations, lead-titanium ratios and isotopic ratios are now regularly used to identify evidence of anthropogenic forcing on the lead biogeochemical cycle. Lead-titanium ratios are used to identify non-silicate sources of lead (Shotyk, 1996; Görres and Frenzel, 1997) whereas isotopic ratios are also considered to reflect accurately anthropogenic lead emissions especially when the isotopic signature of potential sources is well known (Martínez- Cortizas et al., 2002). The record of lead derived from Toddle Moss

presented here should therefore provide a reliable chronological record for past lead deposition on to the bog surface. Notwithstanding the numerous complicating variables that can influence the dispersion of gaseous and particulate pollution from source, bogs located close to industrial sites should provide robust records of emissions from these sites as pollutants are deposited onto the mire surface (Mighall et al., 2002a, b).

Slightly elevated lead concentrations (Figure 3) might well be attributed to mid- to late Bronze Age metallurgical activities: centring on 272 cm and 247 cm (c. 940 cal BC to 670 cal BC) and higher Pb/Ti ratios between 270 and 247 cm (Figure 3). Although the concentrations recorded in the core are low, they are elevated above those recorded below 280 cm and so the trends described here may hint at the possibility of early lead working in the area. The discovery of a stone hammer at Wanlockhead (Pickin, 2008) is indicative of prehistoric mining. This particular stone hammer is very similar typologically to the grooved hammerstones found at the prehistoric copper mine at Alderley Edge (Timberlake & Prag, 2005), which are thought to have been used as crushing and pounding implements. There is no contextual evidence for the stone hammer found at Wanlockhead as it was discovered by a mine manager and the exact location is unknown. Perhaps the strongest evidence for an early insular mining/metallurgical industry in Scotland is provided by the isotopic analysis of Early Bronze Age lead beads from Peeblesshire and West Water Reservoir in the Borders. The data indicates a Scottish Southern uplands source – possibly Leadhills - was exploited (Hunter in Toolis, 2007; Hunter et al., 2006). Taken together these separate strands of archaeological evidence are suggestive of activities possibly

ranging from experimental exploitation on a small scale to more significant activity, which could have produced sufficient amounts of pollution to be recorded in the bog More widely, such activity would have taken place during the mid to late Bronze Age when lead is found in bronze alloys. However, the introduction of lead into bronzes or other copper alloys is rare in northern Britain (Dungworth, 1996) and whilst it points towards a demand for lead, it does not provide convincing evidence of an early insular lead industry in southern Scotland. Indeed, lead is found in the St Andrews Hoard but an analysis of the impurities in the artifacts suggests that some of the metal may have been re-worked or produced from different metal sources that might originate from outside Scotland (Cowie et al., 1998).

For purposes of comparison, the lead isotope ratios of the Toddle Moss peat samples are plotted in Figure 6 beside selected lead ores from other locations in the British Isles, and the major Spanish mines of Rio Tinto and Murcia (Rohl, 1996; Stos Gale *et al*., 1995). Lead isotopic signatures from Flanders Moss and Lindow Moss (cf. Le Roux et al., 2004; Cloy et al., 2005) fall within the cluster of British ores from the Mendips, Alderley Edge, NE Wales and the mines at Leadhills and Wanlockhead. Because of the overlap of the isotopic ratios, it is not possible to attribute the origin of this lead to a particular British ore source (cf. Le Roux et al., 2004; Cloy et al., 2005). Nevertheless, the results clearly show that the lead is likely to be of British origin, as the isotopic values for the British ores are clearly separable from those of the heavily-exploited Spanish sources (Shotyk et al., 1998).

The peat samples from Toddle Moss of the section between 296 and 224 cm clearly fall outside all of the clusters shown in Figure 6. An analysis of galena samples from Wanlockhead has established the isotopic signature for lead ore at this location. Cloy et al. (2005) reported a $^{206}Pb/^{207}Pb$ ratio of 1.172 $\pm$ 0.003, which is in close agreement with a value of 1.170 $\pm$ 0.003 for the Leadhills and Wanlockhead lead ore reported by Sudgen et al. (1993). Rohl (1996) calculated the mean $^{206}Pb/^{207}Pb$ ratio from five ore samples from Wanlockhead plus six from Leadhills as 1.171 $\pm$ 0.001. These values all plot within the 'British ore' cluster (Figure 6). This suggests that the source of lead determined within the Toddle Moss peat samples between 296 and 224 cm does not originate from the main galena bearing lodes from the Leadhills or Wanlockhead orefield. However, one sample of galena from Wanlockhead has a $^{206}Pb/^{207}Pb$ ratio of 1.142 and it is plotted in figure 6 as the 'Wanlockhead outlier.' This ratio is in much better agreement with the Toddle Moss samples between 296 and 224 cm. If early miners and metallurgists did exploit lead at Wanlockhead, then they appear to have targeted lodes bearing a similarlead isotopic signature.

A more extensive analysis of the isotopic signatures of the mineralised zones in the Orefield could resolve the apparent signature discrepancies between the peat samples, the Wanlockhead 'outlier' and the other Leadhills ore samples. Whether the two distinct phases of lead formation at Leadhills resulted in the different isotopic signatures is unknown. The natural lead isotope composition of rocks depends upon the age of the lithogenic system, the U/Pb and Th/Pb ratios of the system and mixing during remobilization and metamorphism (Keinonen, 1992). During the formation of lead ore deposits, lead is separated from the parent

uranium and thorium isotopes, with the lead isotopic composition of hydrothermal fluids being 'frozen' into lead-bearing minerals (Church et al., 1993). Thus, the isotopic composition of a given ore deposit is a function of four parameters: 1) the decay rate of parent isotopes, 2) the initial ratio of the abundance of the parent to the abundance of Pb ($^{238}Pb/^{204}Pb$, $^{232}Th/^{204}Pb$) in the source reservoir (e.g. mantle or continental crust), 3) the initial isotopic composition of reservoir Pb and 4) the duration of reservoir evolution prior to separation of Pb by geological processes (Sangster et al., 2000).

A second phase of increasing lead enrichment and relatively higher Pb/Ti ratios at Toddle Moss occurs during the late Iron Age c. cal BC 365-70 AD (between 219 and 179 cm; Figures 3, 4, 7). Whether this represents pollution generated from local lead extraction or metallurgy is still contestable as there is a lack of local archaeological evidence. However, the shift in the $^{206}Pb/^{207}Pb$ ratio towards values close to those determined from Leadhills and the average value for atmospheric lead in Scotland in the 19th century AD provides evidence of industrial activity within the region at this time. Whilst the initial rise of lead concentrations does correlate quite closely with the suggested age of the Carghidown promontory fort lead beads dated c. cal BC 360-60 AD (Toolis, 2007) these finds are exceptional. Hunter et al. (2006) suggest that circumstantial evidence, such as described earlier including at West Water Reservoir (see above), points to the use of lead sources in prehistory at Leadhills and Tonderghie in Dumfries and Galloway but in general there is very little evidence of native lead use in the Iron Age.

Shifts in the $^{206}Pb/^{207}Pb$ ratios and/or increased lead has been regularly recorded in peat profiles dated to the Late Iron and Roman times (Renberg et al., 2001; De Vleeschouwer et al. 2010). This includes sites in the British Isles: north-west and south west England (Le Roux et al. 2004; Meharg et. al., 2012), central Wales (Mighall et al., 2002b, 2009), at Flanders Moss in central Scotland (Cloy et al., 2005, 2008) and Raeburn Flow in southern Scotland (Küttner et al., 2014). The results suggest that British ores were exploited at least two centuries before the Roman occupation (Cloy et al., 2005) and that Roman exploitation always followed an earlier indigenous (British) lead extraction industry. The equivalent timeframe at Toddle Moss is contained between approximately 182 and 148 cm (AD 40-410; Figure 3). Across this part of the core lead concentrations and Pb/Ti ratios remain low: this is rather unusual. Lead concentrations initially fall and then rise slightly between 150 and 160 cm before declining once again. This small peak may represent small scale, episodic mining/metallurgical activity towards the end of the roman occupation of Britain but a clear phase of enrichment is not observed in contrast to the one recorded during across the Iron Age and Roman transition in peat bog records elsewhere in Scotland and further afield (e.g. Küttner et al., 2014 and references previously cited; Fig 7b). Notwithstanding the coarse resolution of the isotope data, there is an increase in $^{206}Pb/^{207}Pb$ ratio from 1.154 ± 0.0006 at 182-184 cm (c. AD 25) to 1.175 ± 0.0021 at 158-160 cm (c. AD 280) (Figure 3) which is consistent with the mean ratio derived by Rohl (1996) from six galena samples from Leadhills and five from Wanlockhead . However, he low concentrations recorded in the Toddle Moss peat core also imply that local lead ores remained unexploited or that any such activity was small in scale and may have only generated a pollution signal that is

below the level of detection using current methods. Moreover, there is a lack of any definitive local archaeological evidence for lead mining and metallurgy for this period.

The Roman occupation of Scotland was short and intermittent, spanning approximately 150 years between the late 1st and early 3rd centuries AD, with actual occupation by the Roman army occurring over as few as 40 years (Breeze & Dobson, 1996). There is evidence that the Romans were present in the area around Toddle Moss as a Roman road – with associated forts and temporary camps – extended northwards from Carlisle up to Crawford (Fairhurst, 1955; Figure 1). The road passes the Elvanfoot valley which runs westwards to Leadhills and Wanlockhead. There was also a fortlet at Sanquhar to the south west of Leadhills and Wanlockhead. Such a transient occupation may not have allowed or encouraged the development of any large scale mining operation although both Wilson & Flett (1921) and MacDonald et al. (2005) have suggested that lead extraction may have occurred during Roman times. If the gradual rise in lead concentrations between 219 and 176 cm at Toddle Moss does indicate the existence of a local Iron Age lead extraction industry at Leadhills or Wanlockhead another unknown factor possibly acted as a disincentive to further, more expansive Roman exploitation. The rarity of silver in Scotland and northern Britain lead ores may have depreciated its importance. This is in contrast with the record from Raeburn Flow, approximately 74 km to the south east, and at Flanders Moss to the north, where small but more discernible lead contamination occurred during the pre Roman and early part of the Roman period (Küttner et al.,

2014; Cloy et al., 2005) (Fig. 7b,c). However, Raeburn Flow is much closer to the Northern Pennine orefield, the lead and zinc mines in the Caldbeck fells and Carlisle, where there is evidence for lead smelting: all of which could have been pollution sources (Murphy, 2011). Whilst, lead artefacts have been found in both native and Roman contexts during the Roman Iron Age in Scotland, and although the finds suggest some interaction between the Romans and natives, it is still unclear where the objects originated from and who manufactured them (e.g. Hunter, 1996).

Martínez Cortizas et al. (2013) note that records from mires, lakes and lagoons do not always show metal enrichment during the late Iron Age and Roman period. For example, some studies, such as those from southern France (Labonne et al., 1998), the Eifel area and Ireland (Schettler & Romer, 2006) do not show any evidence of contamination during the Iron Age whilst mires from Bavaria (Küster & Rehfuess, 1997), central and south-eastern France (Monna et al., 2004; Baron et al., 2005) also show no metal enrichment during the Roman period. The Toddle Moss record provides additional evidence for specific regional variations in the evolution of mining and metallurgy during prehistoric and Roman times across Europe (cf Martínez Cortizas et al. 2013).

The results suggest phases of enhanced chromium accumulation occurred between 191 and 161 cm (c. 60 cal BC to AD 225) and from 135 to 79 cm (c. AD 550-1150)

Chromium was first discovered in the eighteenth century so it is unlikely to have been intentionally exploited until then (Jacobs and Testa, 2005). Its occurrence in the Toddle Moss record is possibly as a by product of mining, although lead concentrations were low at this time suggesting that little or no mining took place locally, or it is deposited as dust produced from wider land use changes as a proportion of the changes in chromium is also correlated to Cp2 indicating a geogenic contribution. Chromium is relatively enriched in bedrock regionally (MacDonald et al., 2005).

Despite the low concentrations, the lead record between AD 400 and 1610 appears to document the rise of the extraction and metalworking industry. The $^{206}Pb/^{207}Pb$ ratios initially drop to 1.163 $\pm$ 0.0010 at 126-128 cm (c. AD 655) but then return to more radiogenic values thereafter: values of 1.17 and 1.18 from 112 (c. AD 800) to 25 cm (c. AD 1750) (Figure 5) are consistent with the isotopic values determined for galena at both Leadhills and Wanlockhead. The pollution component identified by PCA (Cp1) shows three peaks in the period AD 400-1610, supported by increased lead concentrations and Pb/Ti ratios, pointing to small scale mining/ metallurgical activity at Leadhills/ Wanlockhead during the 5^{th}-7^{th} and 9^{th}-11^{th} centuries AD (Figures 3, 4 & 6). The first peak occurs at 133 cm (c. AD 572, with a short-lived peak in Cp1 and Cp1-PI cores, lead concentrations and Pb/Ti ratio. Lead shows a sustained rise after c. AD 900 (103 cm) as the $^{206}Pb/^{207}Pb$ ratio increases to 1.173 $\pm$ 0.0010 (106-108 cm, c. AD 855). Lead peaks at 93 cm (c. AD 1010) along with a peak in the Pb/Ti ratio, subsequently falls (to 85 cm) before increasing again to 65 cm (c. AD 1310). Charcoal, taken from a lead slag scatter at Glennkip in the Leadhills, has been

radiocarbon dated to the early 11th century AD, whilst smelting sites date to the late 10th and 11th centuries at Manor Valley (Pickin, 2010). Whilst the first record for lead mining in the Leadhills district is provided by the Monks of Newbattle dated to AD 1239 (Wilson & Flett, 1921), the series of small but discernible peaks throughout the early medieval period .

After AD 1310, there is a gradual decrease in the Toddle Moss lead concentrations. This trend continues up the core to 50 cm (c. AD 1475). This coincides with the timing of the Anglo-Scottish war, a period for which there is no documentary accounts of lead mining in Leadhills/ Wanlockhead. Written records recommence from AD 1466. After this date the lead concentrations in the peat slowly begin to rise, possibly in response to the establishment of post medieval smelting mills in the upper reaches of Glengonnar and Wanlockhead Water (Pickin, 2010).

Lead, arsenic, chromium and zinc concentrations all increase above 38 cm (c. AD 1610) (Figures 3, 4). The expansion in lead mines at Leadhills and Wanlockhead is well-documented for the 17th century, with peak activity occurring between AD 1850 and1920. Through this part of the peat record (24 cm and above), the $^{206}Pb/^{207}Pb$ ratio generally falls within the range 1.17-1.18. This range is consistent with the isotopic signature of indigenous lead ore smelting from Leadhills and Wanlockhead (Figure 6), and coal combustion ($^{206}Pb/^{207}Pb$ ratio of 1.181) as recorded elsewhere in Scotland (e.g. Farmer *et al.*, 2005; Cloy *et al.*, 2005). A double peak in lead concentrations, dated to the latter part of the 18th and late 19th/early 20thcenturies respectively, is shown. The date of the uppermost peak is consistent with total lead

concentrations measured in a channel bank in Glengonnar Water and average production figures from Leadhills (Rowan et al., 1995).

Increased concentrations of zinc,arsenic and to a lesser extent gallium are most likely to be associated with lead mining, coal combustion (Shotyk et al., 1996; Oremland & Stolz, 2003; Rothwell et al., 2009) and/or plant uptake (Zaccone et al., 2008). . (Coal was used as fuel for lead smelting from AD1727 and small amounts of copper and zinc were also extracted locally (Wilson & Flett, 1921). Chromium is also used as an alloy in steel making (Jacobs & Testa, 2005).

The marked reduction of lead, arsenic, chromium and gallium concentrations in the top 10 cm reflects the demise of the Leadhills and Wanlockhead mines in the 1930s and the subsequent phasing out of leaded gasoline. Less radiogenic $^{206}Pb/^{207}Pb$ ratios once again fall close to the isotopic ratio of the Wanlockhead outlier (Figure 6).
These values reflect a change in the source of the lead deposited on to the bog, with the final closure of the mines and the loss of the main Leadhills isotopic signature, the increasing influence of imported Australian lead ($^{206}Pb/^{207}Pb$ ratio = 1.04) and other alkyl lead additives in petrol which are also phased out in the recent past. These sources would dilute any remnant lead deposition from the Leadhills galena ores. These trends are commonly recorded in bogs across the British Isles (e.g. Cloy et al., 2008; Farmer et al., 1997; Le Roux et al., 2004; Mighall et al., 2002b, 2004, 2009; West et al., 1997). The acrotelm is also affected by ongoing peat forming processes such as decomposition, plant uptake/recycling, element mobility and fluctuations at the acrotelm/catotelm transition. These processes may also have

played a role in influencing the distribution of elements through the peat such as zinc (Jones, 1987; Shotyk, 1988; Espi et al. 1997; Biester et al., 2012).

Conclusions

The Toddle Moss record provides evidence of three major phases of atmospheric metal contamination which accord well with historical and archaeological records of mining and metallurgy from medieval times to present: 5-7th centuries AD, 9th-11th centuries AD and the latter part of the 18th and late 19th/early 20thcenturies respectively. No evidence of major Roman activity was discovered and provides further evidence for specific regional variations in the evolution of mining and metallurgy and an associated contamination signal in Roman times across Europe. Patterns of lead might reflect earlier activity during the Bronze and Iron Ages but further analysis will be required to confirm if the Leadhills/Wanlockhead was an early source of metals as part of an insular metal mining industry.

Acknowledgements

Thanks to Nathan Pittam, Claire Devonport and Alice Humphries for help with fieldwork. Coventry University and Society of Antiquaries of Scotland kindly provided funding. We thank Joanna Cloy and John Farmer for provision of lead isotope data and for helpful comments. Jason Jordan prepared some of the material for analysis. Thanks to David Cranstone for information about lead sources. We thank Alison Sandison and Jenny Johnson at the University of Aberdeen for cartographical support. Peter Gayford (Hopetoun Estates) and James C E Hodge kindly gave

permission to take a core from Toddle Moss. We would like to thank the two anonymous reviewers for their considered and useful comments.

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Figure and Table captions

Fig. 1. (A) Location of study area in Britain (B) Location of Leadhills, Wanlockhead, and Toddle Moss, (C) Evidence of early leadworking after Pickin, 2010). The place name 'bail' is considered to indicate a lead smelting site.

Fig 2: An age-depth model for Toddle Moss using Clam (after Blaauw, 2010).

Fig. 3: Calcium/Magnesium ratio (by ICP-OES), Titanium concentrations, Lead concentrations (by EMMA; dashed line on a log scale), Pb/Ti ratio and $^{206}Pb/^{207}Pb$ ratios (by ICP-MS) from Toddle Moss. Dashed line represents exaggerated Pb/Ti ratios from 40 cm down the profile (scale at base of the graph).

Fig. 4. Concentrations of lead, arsenic, gallium, yttrium, zinc and chromium as determined by EMMA. Dashed line - lead plotted on a logarithmic scale (scale at base of the graph).

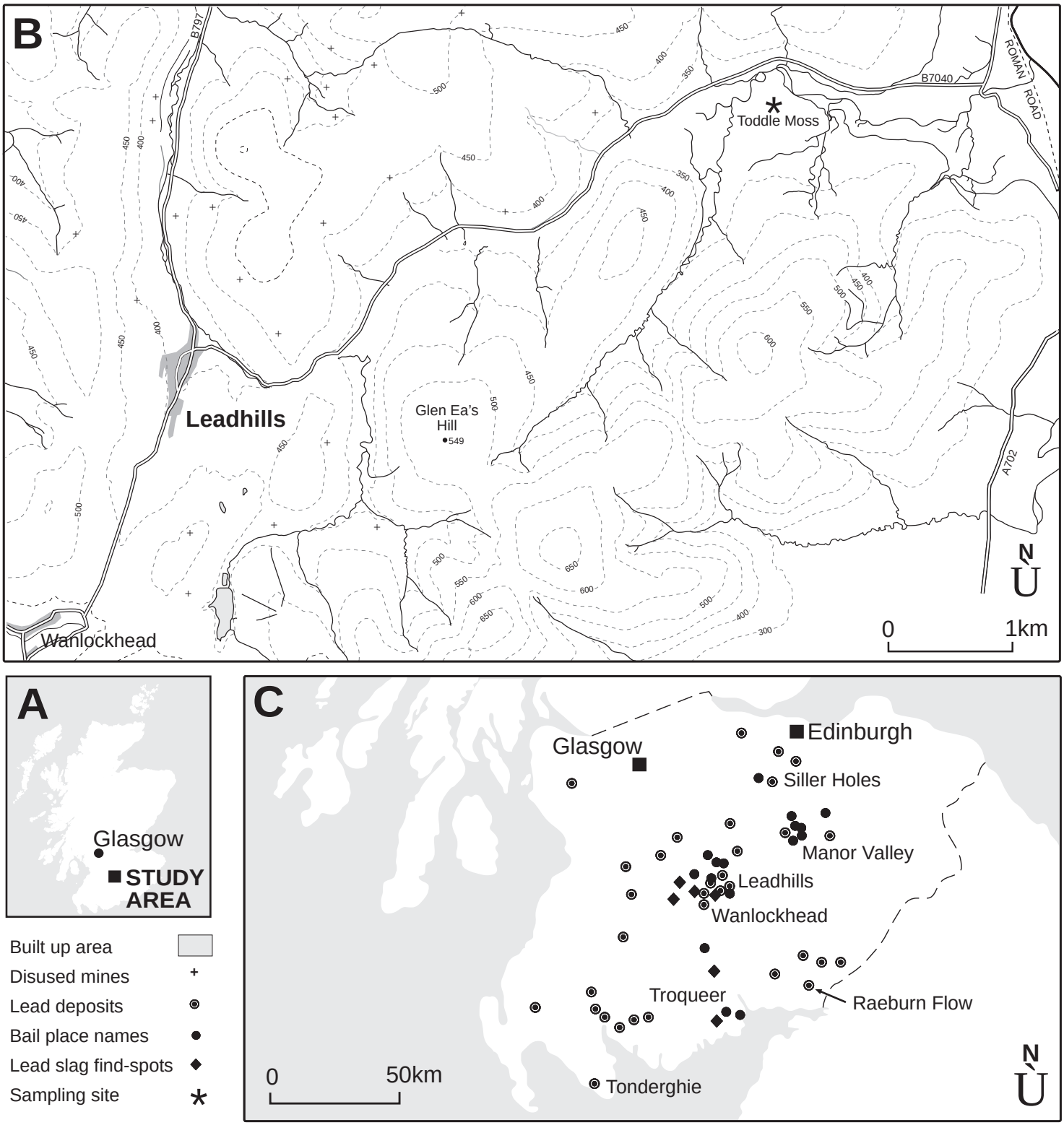
Fig. 5. Records of scores of the extracted principal components. Cp1 and Cp2, are the components extracted using the whole data set; Cp2-PI, corresponds to a component characterized by high Zn, As and Cr loadings extracted using data for pre-industrial peat sections. The second panel from the left shows the Cp1 scores without the superficial samples (note that, as indicated in the text, these scores are essentially the same as those of Cp1-P1, r 0.97).

Fig. 6. Plot of $^{208}Pb/^{206}Pb$ *versus* $^{206}Pb/^{207}Pb$ ratios from samples from the Toddle Moss core and galena from various British and Spanish ores. Data from Rohl (1996) and Stos Gale et al. (1995).

Fig. 7. Comparison of lead records from selected peat bogs in Scotland; (a) Leadhils lead concentrations and Pb/Ti ratio; Dashed line represents exaggerated values down the profile (scale at base of the graph). (b) Raeburn Flow lead concentrations and lead enrichment factor. Enrichment factor is calculated using the equation proposed by Shotyk (1996). Titanium was used as the reference lithogenic element (from, and full details in, Kuttner *et al*. 2014) Dashed lines represent exaggerated values down the profiles (scale at base of the graph); (c) Flanders Moss lead concentrations (from, and full details in, Cloy *et al*. 2005).

Table 1. Radiocarbon dates from Toddle Moss.

Table 2. Loadings of the variables in the components extracted by PCA on the chemical composition of the peat. Cp1 and Cp2, components extracted using the whole data set; Cp1-PI to Cp3-PI, components extracted using data for pre-industrial peat sections. Eigv: eigenvalues, Var: percentage of total variance, Com: communality (proportion of variance of each element explained by the two principal components).


B
B797
B7040
ROMAN ROAD
A702
Toddle Moss
Leadhills
Glen Ea's Hill
549
Wanlockhead
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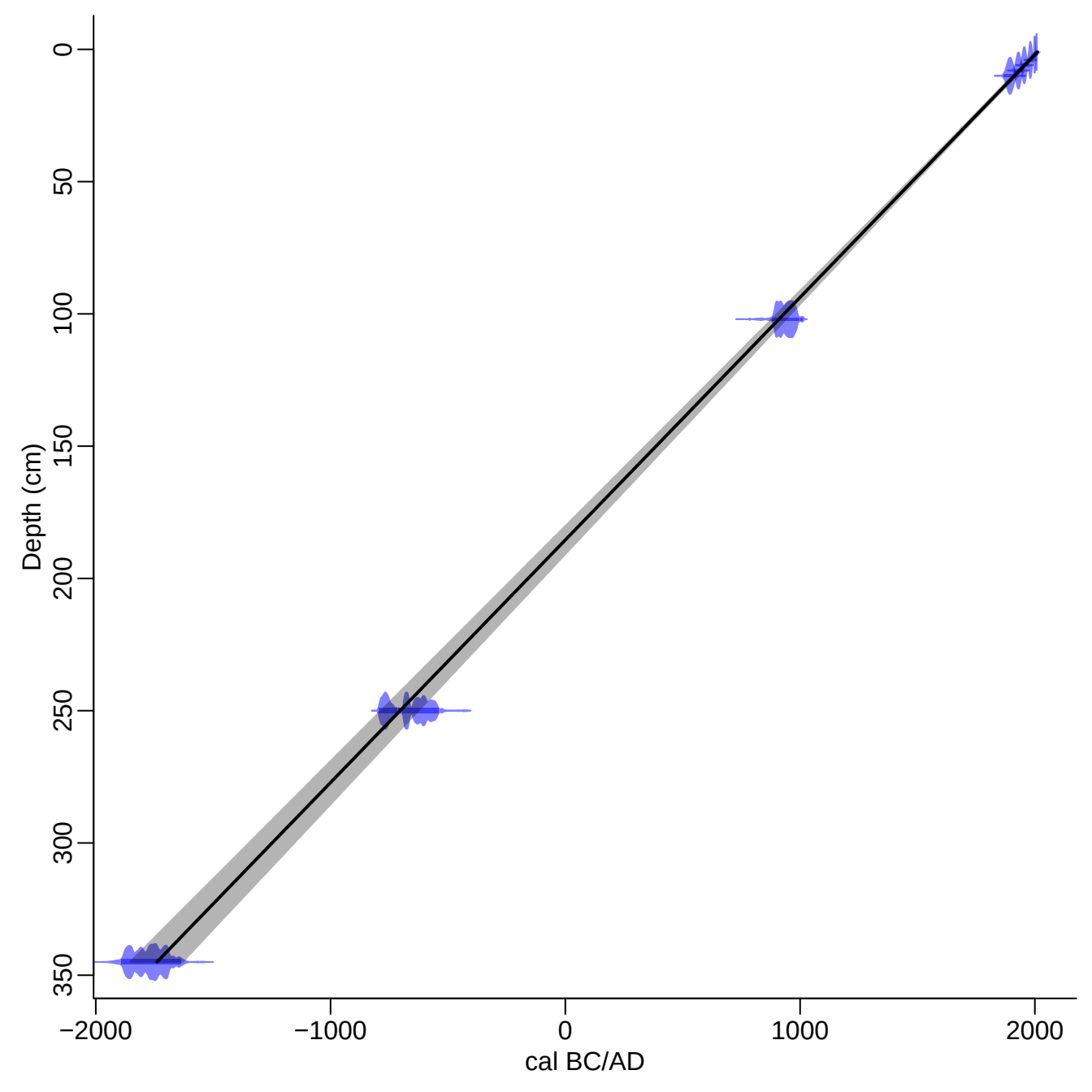
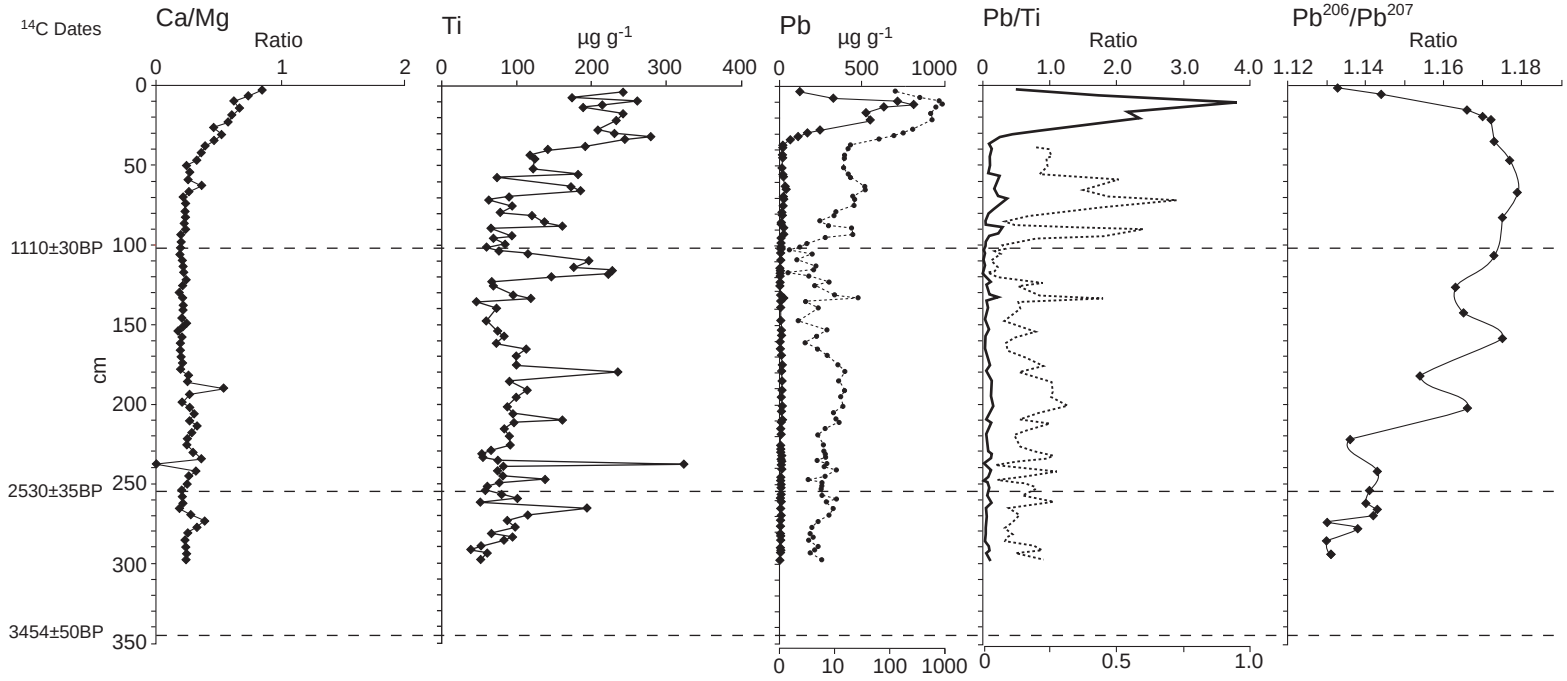
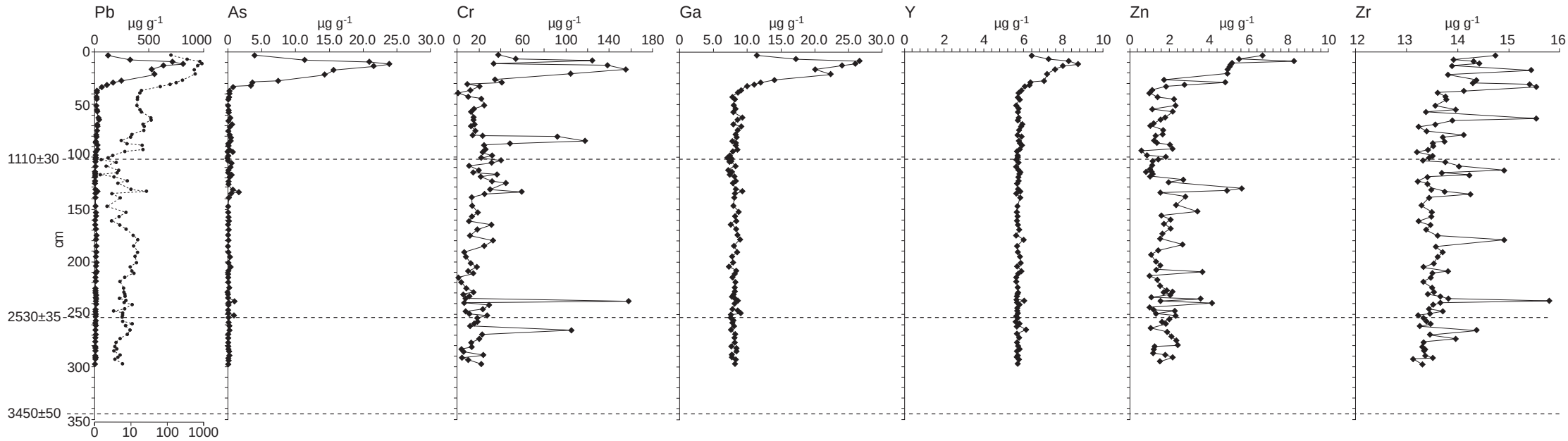
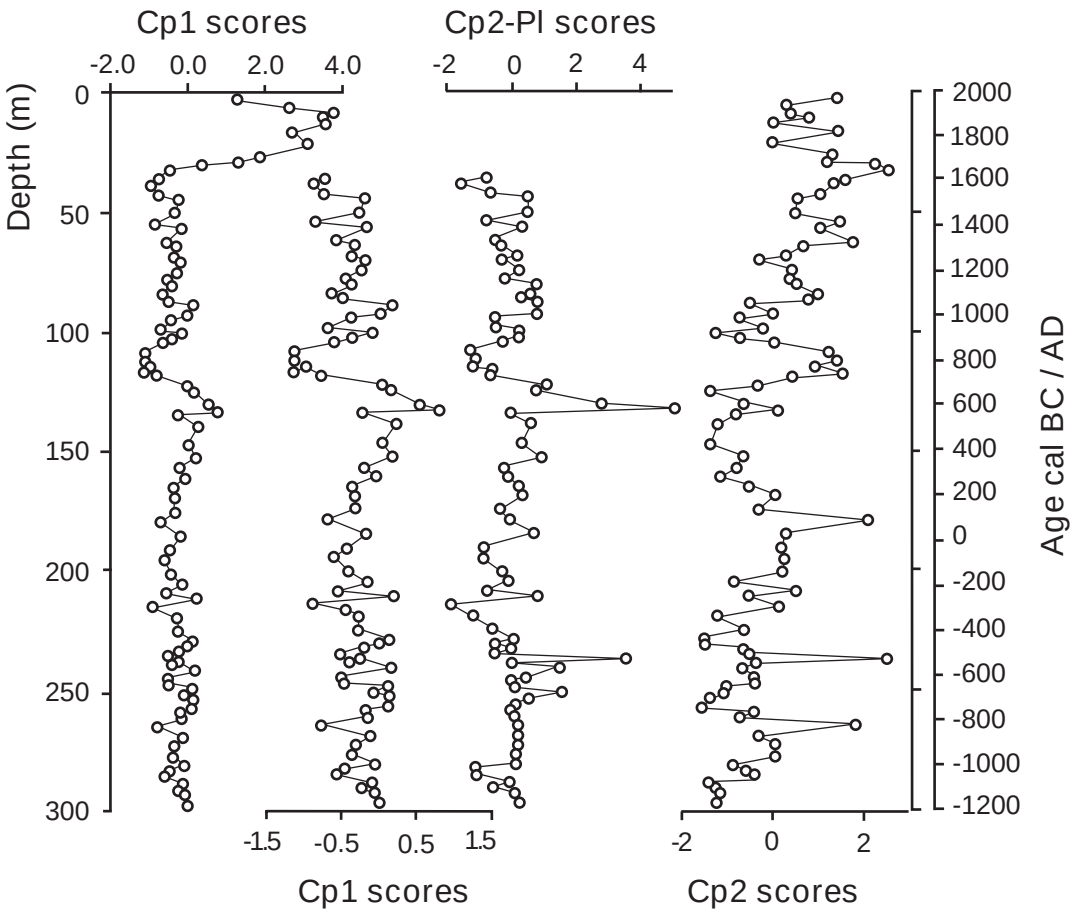
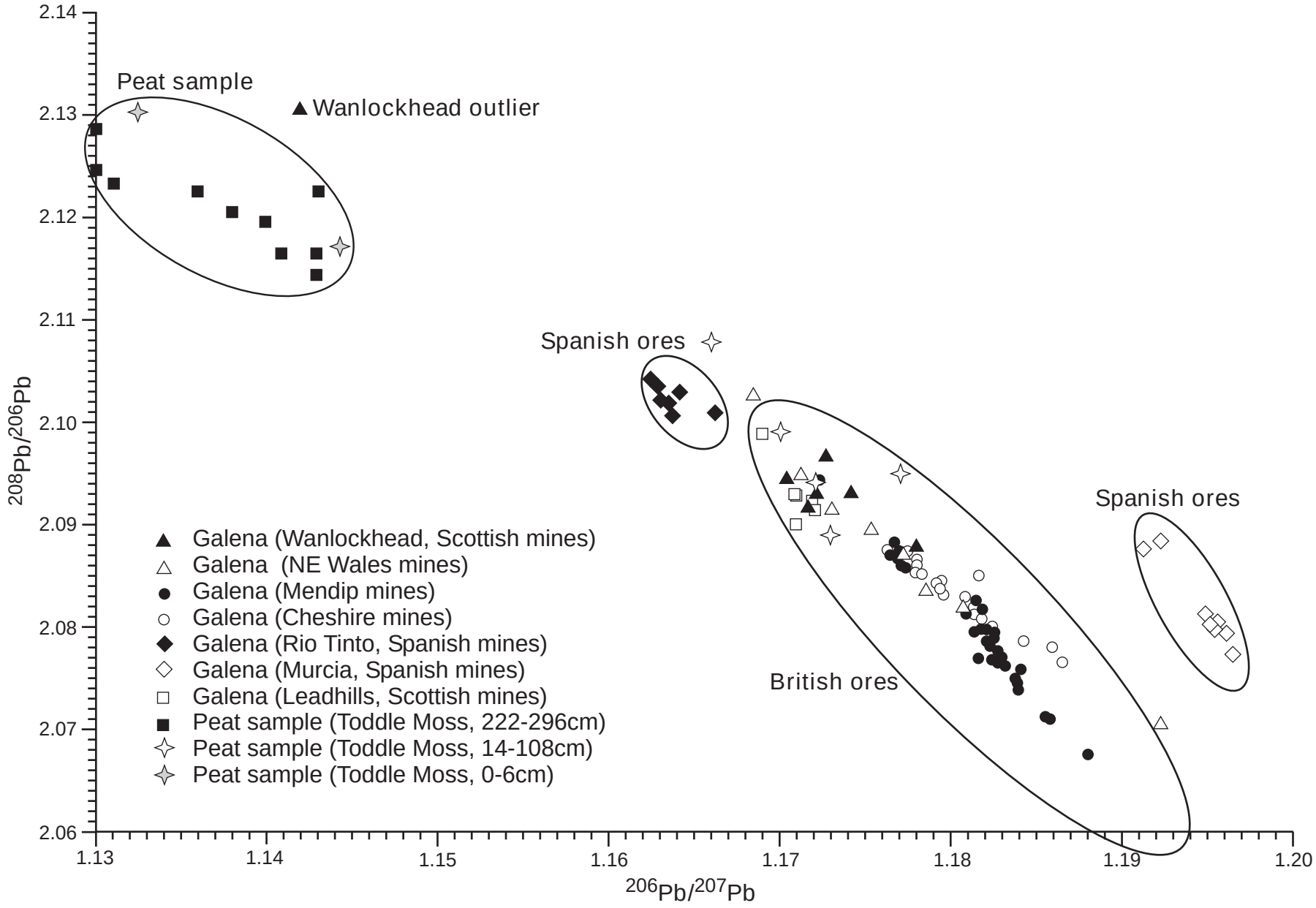
STUDY AREA
Built up area
Disused mines
Lead deposits
Bail place names
Lead slag find-spots
Sampling site
C
Glasgow
Edinburgh
Siller Holes
Manor Valley
Leadhills
Wanlockhead
Troqueer
Raeburn Flow
Tonderghie
0
50km
N


Depth (cm)
0
50
100
150
200
250
300
350
−2000
−1000
0
1000
2000
cal BC/AD


14C Dates
Ca/Mg
Ratio
0
1
2
Ti
µg g-1
0
100
200
300
400
Pb
µg g-1
0
500
1000
Pb/Ti
Ratio
0
1.0
2.0
3.0
4.0
Pb206/Pb207
Ratio
1.12
1.14
1.16
1.18
cm
0
50
100
150
200
250
300
350
1110±30BP
2530±35BP
3454±50BP
0
10
100
1000
0
0.5
1.0


Pb
As
Cr
Ga
Y
Zn
Zr
µg g-1
cm
0
50
100
150
200
250
300
350
1110±30
2530±35
3450±50
0 500 1000
0 5.0 10.0 15.0 20.0 25.0 30.0
0 20 60 100 140 180
0 5.0 10.0 15.0 20.0 25.0 30.0
0 2 4 6 8 10
0 2 4 6 8 10
12 13 14 15 16
0 10 100 1000


Cp1 scores
-2.0
0.0
2.0
4.0
Cp2-Pl scores
-2
0
2
4
Depth (m)
0
50
100
150
200
250
300
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
-1000
-1200
Age cal BC / AD
-1.5
-0.5
0.5
1.5
Cp1 scores
-2
0
2
Cp2 scores


Peat sample
Wanlockhead outlier
Spanish ores
Spanish ores
British ores
Galena (Wanlockhead, Scottish mines)
Galena (NE Wales mines)
Galena (Mendip mines)
Galena (Cheshire mines)
Galena (Rio Tinto, Spanish mines)
Galena (Murcia, Spanish mines)
Galena (Leadhills, Scottish mines)
Peat sample (Toddle Moss, 222-296cm)
Peat sample (Toddle Moss, 14-108cm)
Peat sample (Toddle Moss, 0-6cm)
2.14
2.13
2.12
2.11
2.10
2.09
2.08
2.07
2.06
208Pb/206Pb
1.13
1.14
1.15
1.16
1.17
1.18
1.19
1.20
206Pb/207Pb

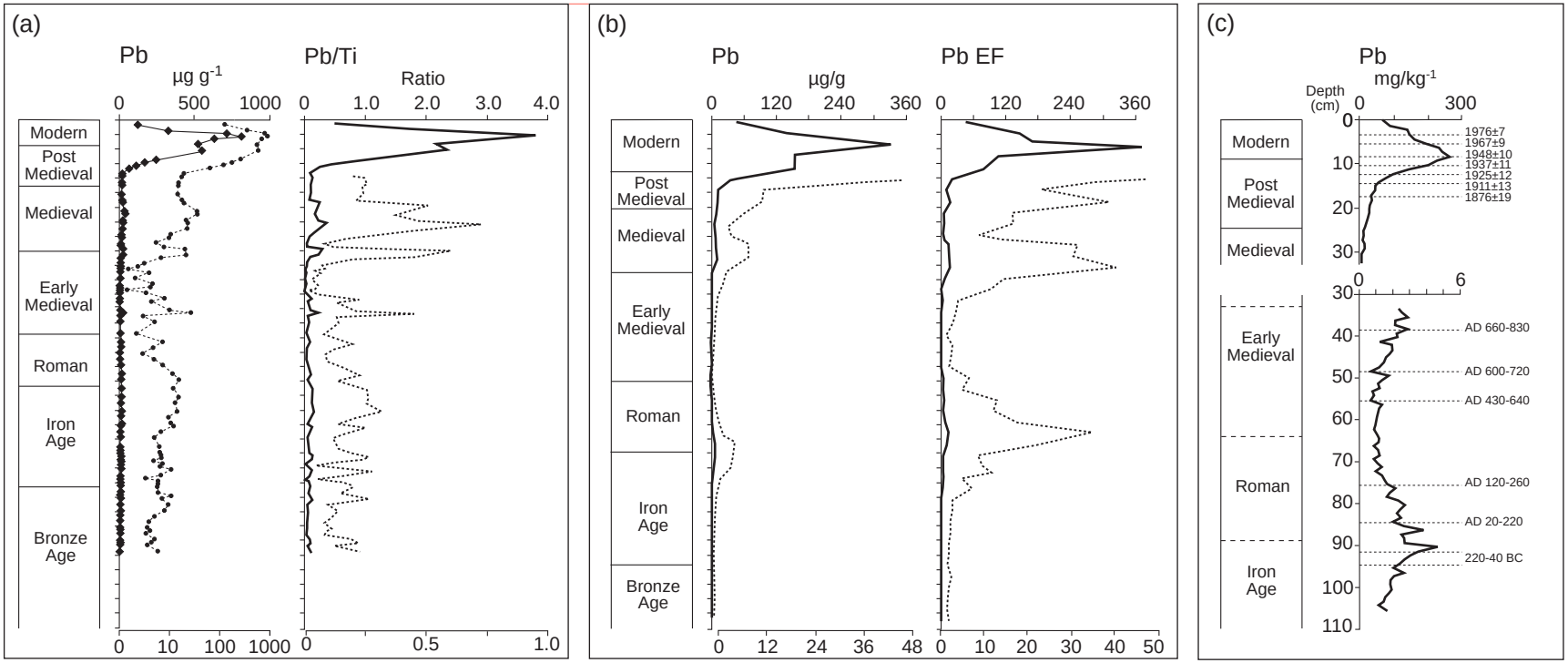

(a)
Pb
µg g-1
0
500
1000
Pb/Ti
Ratio
0
1.0
2.0
3.0
4.0
Modern
Post Medieval
Medieval
Early Medieval
Roman
Iron Age
Bronze Age
0
10
100
1000
0
0.5
1.0
(b)
Pb
µg/g
0
120
240
360
Pb EF
0
120
240
360
Modern
Post Medieval
Medieval
Early Medieval
Roman
Iron Age
Bronze Age
0
12
24
36
48
0
10
20
30
40
50
(c)
Pb
mg/kg-1
Depth (cm)
0
300
1976±7
1967±9
1948±10
1937±11
1925±12
1911±13
1876±19
Modern
Post Medieval
Medieval
Early Medieval
Roman
Iron Age
0
10
20
30
0
6
30
40
50
60
70
80
90
100
110
AD 660-830
AD 600-720
AD 430-640
AD 120-260
AD 20-220
220-40 BC

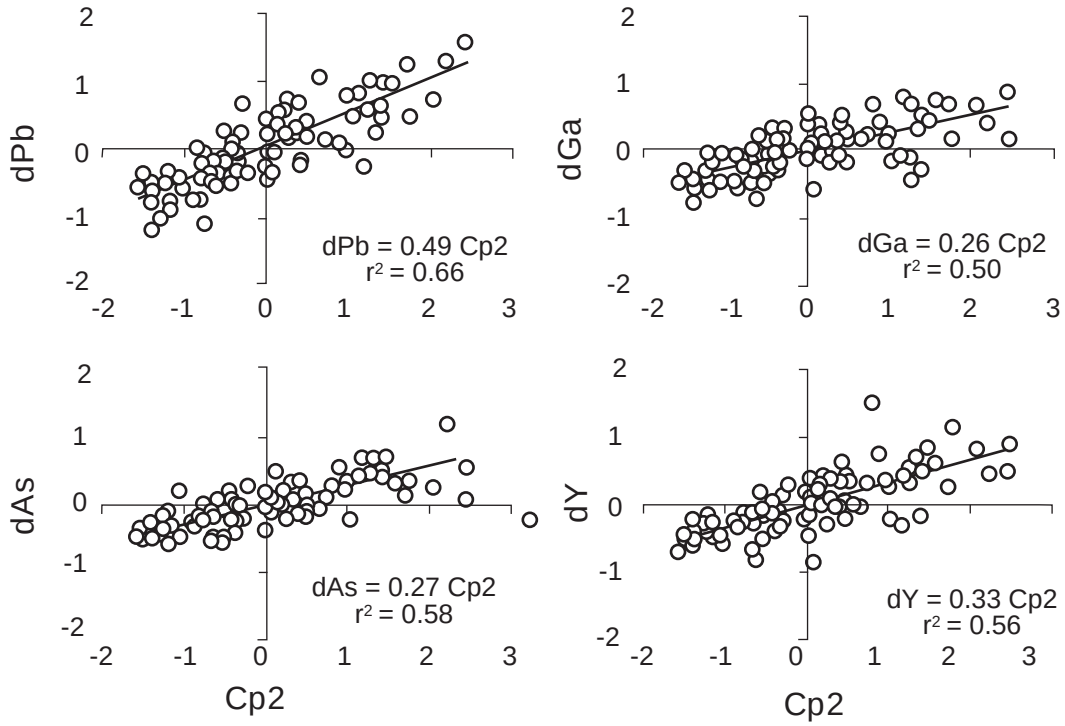
Table 1. Radiocarbon dates from Toddle Moss.

Lab code	Sample	Depth (cm)	uncalibrated age	calibrated age range (2σ)
Poz-56748	Sphagnum leaves	102-103	1110±30	cal AD 879-1013
Poz-19215	Peat	250-252	2530±35	cal BC 797-539
Beta-15142	Peat	345	3450±50	cal BC 1890-1634

Table 2. Loadings of the variables in the components extracted by PCA on the chemical composition of the peat. Cp1 and Cp2, components extracted using the whole data set; Cp1-PI to Cp3-PI, components extracted using data for pre-industrial peat sections. Eigv: eigenvalues, Var: percentage of total variance, Com: communality (proportion of variance of each element explained by the two principal components).

	Cp1	Cp2	Com		Cp1-PI	Cp2-PI	Cp3-PI	Com
As	**0.93**	0.27	0.95	**Si**	**0.83**	0.08	0.15	0.71
Ga	**0.93**	0.26	0.93	**Ti**	**0.83**	-0.18	0.03	0.72
Y	**0.90**	0.33	0.91	**Al**	**0.79**	0.04	0.21	0.67
Zn	**0.82**	0.05	0.67	**Y**	**0.71**	0.15	0.06	0.53
Pb	**0.82**	0.43	0.85	**Zr**	**0.69**	-0.16	0.06	0.51
Cr	**0.51**	0.35	0.38	**Zn**	-0.27	**0.75**	0.25	0.69
Ti	0.29	**0.86**	0.83	**As**	0.04	**0.74**	0.13	0.56
Si	0.35	**0.85**	0.83	**Cr**	0.44	**0.59**	-0.54	0.83
Al	0.15	**0.84**	0.73	**Ga**	0.16	0.18	**0.83**	0.74
Zr	0.21	**0.80**	0.69	**Pb**	0.43	0.23	**0.67**	0.69
Eigv	4.40	3.37		**Eigv**	3.45	1.63	1.58	
Var	44.0	33.7		**Var**	34.5	16.3	15.8	

SI Table 1. Lead isotopic measurements from Toddle Moss.


dPb
dPb = 0.49 Cp2
r² = 0.66
dGa
dGa = 0.26 Cp2
r² = 0.50
dAs
dAs = 0.27 Cp2
r² = 0.58
dY
dY = 0.33 Cp2
r² = 0.56
Cp2
Cp2